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**Title of Project:** Experimental Investigation of Optical Nonlinearities in Conjugated Polymers

**Contract No:** F49620-93-1-0554 [September 30, 1993 - August 31, 1994]

**Author of Report:** G.I. Stegeman, Center for Research and Education in Optics and Lasers (CREOL), University of Central Florida

**Subject Terms:** Nonlinear optics in polymers, nonlinear organics, nonlinear organic devices, nonlinear material characterization

**Personnel:** Professor George Stegeman (Faculty, Cobb-Hooker Chair); Dr. William Torruellas (Postdoctoral fellow); Brian Lawrence (Graduate student); Maria Angeles Diaz Garcia (visitor)

### Executive Summary of Achievements:

The nonlinear optics of sublimated films of 2-dimensional conjugated planar molecules has been investigated by third harmonic generation. Two were planar phthalocyanines, metal-free and copper substituted, and the third was an asymmetric (non-planar) phthalocyanine (subphthalocyanine), employed as a precursor in the synthesis of certain phthalocyanines. A very rich spectrum has been observed in each case and the analysis is currently underway. In the future this work will be expanded to include other materials.

### Detailed Research Achievements:

The third harmonic spectrum of three phthalocyanines (Pc) was measured over the spectral range 900 - 2000 nm. The material in sublimated film form was supplied by Professor D. Fernando Agullo Lopez of the "Instituto Universitario de Ciencia de Materiales "Nicolas Cabrera" of the Universidad Autonoma de Madrid. Investigated were  $\text{PcH}_2$ ,  $\text{PcCu}$  and asymmetric subPc.

The results for the planar molecules are shown in Figs. 1-6. The total phase changes are shown in Figs. 3 and 4. They are amongst the largest that we have observed in any of our previous studies. This indicates that there are at least three, and possibly four strong resonances contributing. The complicated structure obtained for the magnitude  $|\chi^{(3)}(3\omega)|$  also indicated a minimum of three contributing resonances. The two strongest are due to the Q- and B-bands, as expected. Therefore there is at least one contributing two photon state, whose resonance is located between the two one photon bands. Based on the phase changes, for  $\text{PcH}_2$ , there could be at least a pair of two photon states located around 650 and 800 nm. However, there is no strong evidence for these states in the magnitude of  $\chi^{(3)}(3\omega)$ . There are peaks in the THG spectrum of  $\text{PcCu}$  which correspond to these general locations. Therefore the number of "essential states", 4-5, is clearly larger than for linear polyenes and conjugated polymers. The detailed analysis should prove interesting!

The THG spectrum of the asymmetric phthalocyanine is also dominated by the Q-band (now shifted to 580 nm) and the B-band. Again there is evidence for a two photon state around 600 nm.

A disappointing feature is that the magnitude of  $\chi^{(3)}$  is much less than for the polyenes ( $\beta$ -carotene) and linear conjugated polymers (poly4-BCMU and polythiophene) that we have studied previously. The magnitudes were measured relative to glass. However it is noteworthy that phthalocyanines with much larger NLO coefficients have been reported and are worth investigating, for example VOPc and  $\text{Sc(Pc)}_2$ . Also note that substituting the so-called free phthalocyanine  $\text{PcH}_2$

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with Cu does not enhance the third order response. However, going to an asymmetric structure, whith a smaller molecular volume, gives a factor of 5 enhancement.

**Publications:** none (yet)

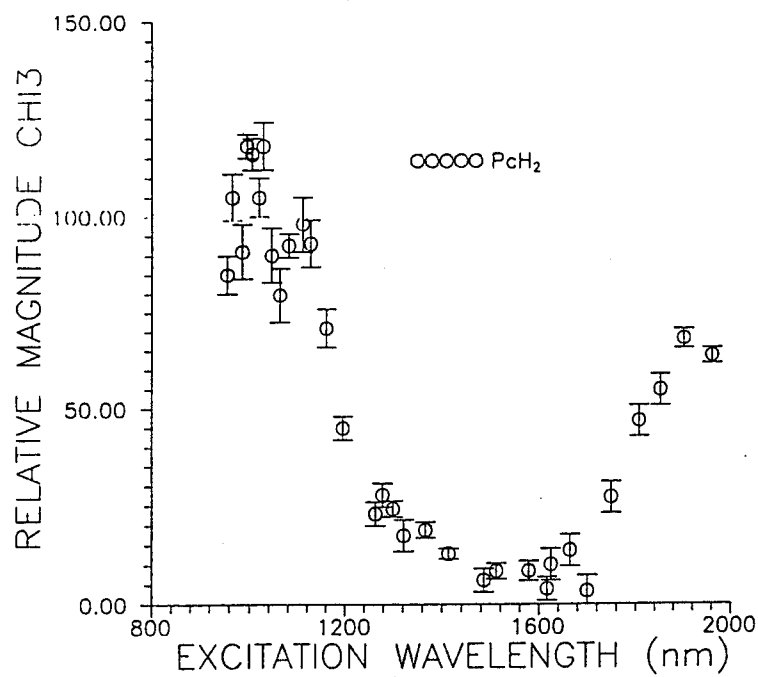


Fig. 1 The modulus  $|\chi^{(3)}(3\omega)|$  for hydrogen phthalocyanine relative to fused silica.

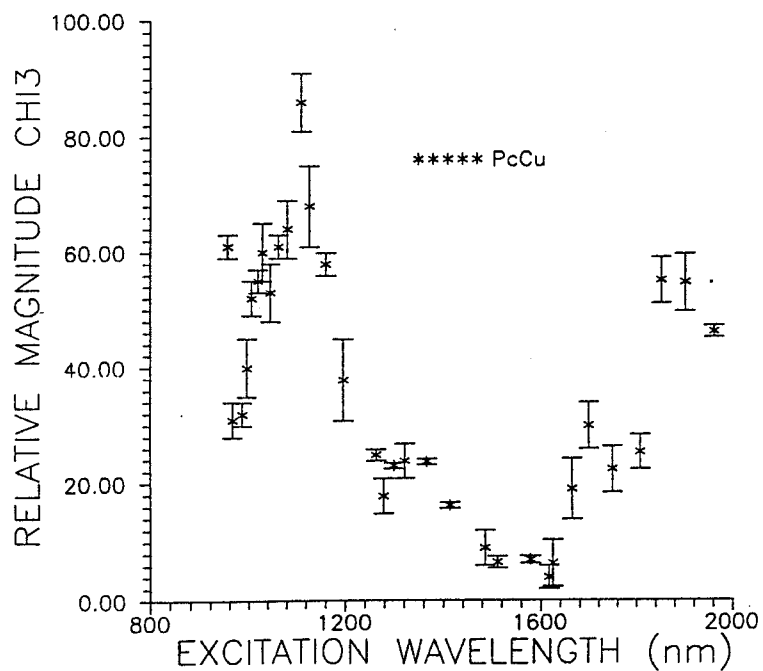


Fig. 2 The modulus  $|\chi^{(3)}(3\omega)|$  for copper phthalocyanine relative to fused silica.

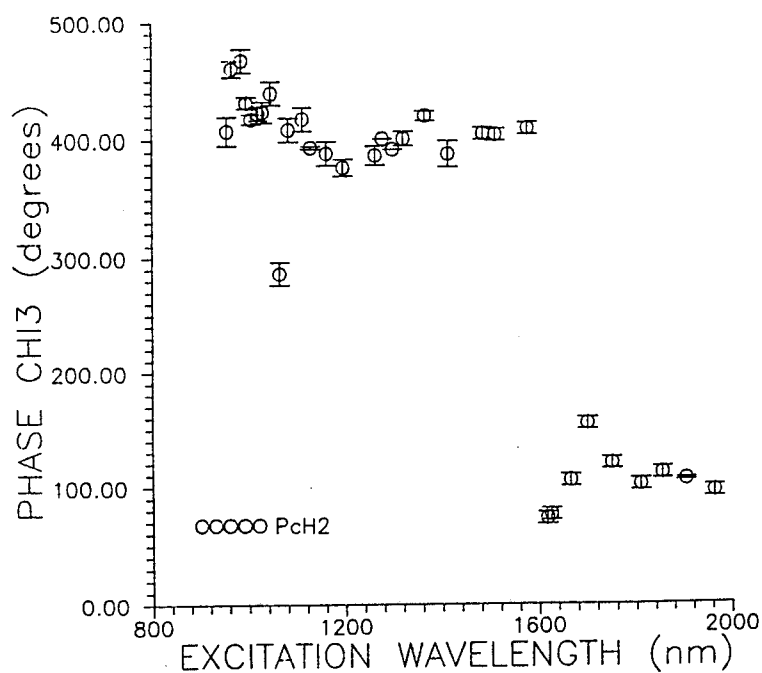


Fig. 3 The phase of  $\chi^{(3)}(3\omega)$  for hydrogen phthalocyanine (O), measured relative to the fused silica substrates.

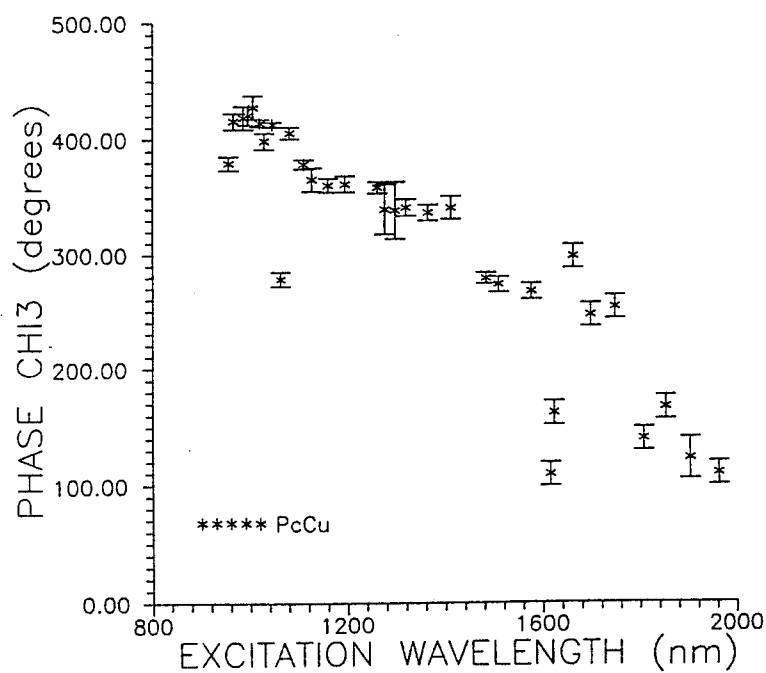


Fig. 4 The phase of  $\chi^{(3)}(3\omega)$  for, copper phthalocyanine (\*), measured relative to the fused silica substrates.

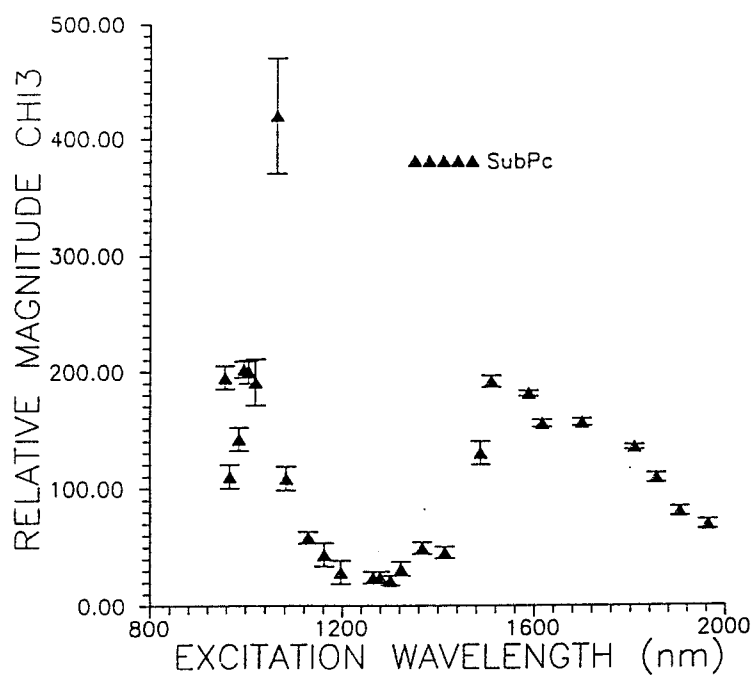


Fig. 5 The modulus  $|\chi^{(3)}(3\omega)|$  for the asymmetric phthalocyanine relative to fused silica.

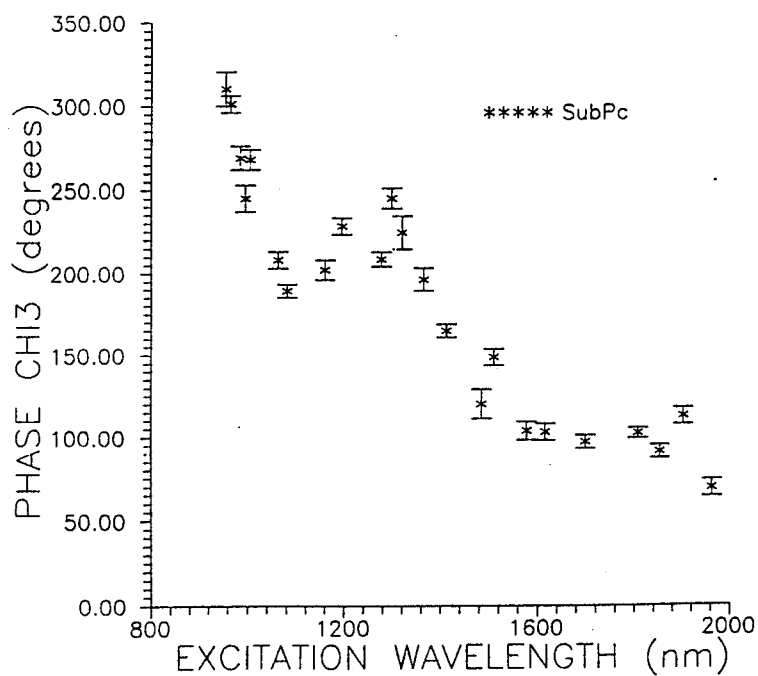


Fig. 6 The phase of  $\chi^{(3)}(3\omega)$  for the asymmetric phthalocyanine, measured relative to the fused silica substrates.